Effects of Gold Colloid and KO on the Formation of Lithium Metasilicate Crystallites in Photosensitive Opal Glass

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Effects of Gold Colloid and K_2O on the Formation of Lithium Metasilicate Crystallites in Photosensitive Opal Glass

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Normally, from chemically mashinable photosensitive opal glasses lithium metasilicate crystal but not lithium disilicate crystal is separated out upon reheating. In order to investigate its cause, lithium silicate glasses with small amounts of gold and K_2O have been prepared, and their crystallization temperatures have been measured by DTA technique. The cryatals separated out from the glasses upon reheating have also been identified by X-ray diffraction technique. The results obtained are summarized as follows:

(1) The crystallization temperature for the lithium silicate glasses rises proportionately with the increase of the K_2O/Li_2O (by mol.%) ratio of the glasses.

(2) The crystallization temperature for the glasses is much lowered by the addition of 0.005 mol.% gold colloids.

(3) The lithium metasilicate crystals are separated out upon reheating even from the glasses whose ratio of Li_2O/SiO_2 is less than 1/2, if the glasses contain K_2O higher than 1 mol.% together with gold of 0.005 mol.%.

The explanations from the above mentioned phenomena have been drawn on the basis of the concept that (a) the Si-O bonds in the Li-Si-O groups are weakened by the polarizable single bonded oxygens associated with Li^{+1} ions, and (b) the polarizable single-bonded oxygens are absorbed at the surface of gold colloids together with the Li^{+1} ions.

INTRODUCTION

From lithium silicate glasses bearing of $Li_2O \cdot 2$ to $4SiO_2$ composition lithium disilicate crystals ($Li_2Si_2O_5$) ordinarily precipitate upon their reheating. Rindone[1] has studied the nucleating effects of platinum on the crystallization of a glass of $Li_2O \cdot 4SiO_2$ composition and determined the rate of formation of $Li_2Si_2O_5$ crystals from the glass as a function of platinum concentration at 600°C and 650°C. Matveev and Velya[2] have investigated the homogeneous crystallization of lithium silicate glasses having various compositions from $Li_2O \cdot 2SiO_2$ to $Li_2O \cdot 6SiO_2$, and found that solid solutions of silica in lithium disilicate separates out from the glasses of $Li_2O \cdot 3$ to $6SiO_2$ compositions. Sakka and Tashiro[3] have studied the effect of addition of various oxides on the crystallization of a lithium silicate glass and showed that their addition retards the precipitation of $Li_2Si_2O_5$ crystals from the glass in proportion to the polarizing power of the cations in the oxides added.

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Cases are known, however, in which lithium metasilicate crystals (Li_2SiO_3) separate out from the glasses containing less Li_2O than that of the $Li_2O \cdot 2SiO_2$ composition. For example, Stookey[4] has discovered the formation of Li_2SiO_3 crystals in lithium silicate photosensitive glasses added with minor amount of potassium oxide ($70 \sim 80SiO_2$, $9 \sim 15Li_2O$, $0 \sim 8Na_2O$ or K_2O, $0.001 \sim 0.03$Au and $0 \sim 0.05$ wt. per cent CeO_2) when nucleated by photographic precipitation of metallic colloids of gold, silver or copper. Stookey[5] had ever once stated in his report on the crystallization of glass that generally, in the process of heterogeneous crystallization of glasses, a crystal whose crystal structure and lattice parameter are similiar to those of the nucleating catalyst first precipitates on the surface of the catalyst. This statement, however, can not be applied to the peculiar phenomenon above mentioned, because, if so, there must have been a possibility of formation of Li_2SiO_3 crystals also in the lithium silicate glasses containing platinum colloids whose lattice parameter is almost similar to that of gold: The experimental results obtained by Rindone etc. showed no formation of the Li_2SiO_3 crystals as described above.

This fact has led the authors to consider if there might be some other more potent factors which determine the type of crystal formed in the photosensitive glass, and further to assume that the K_2O component in the presence of gold colloid would be one of the factors. In order to ensure this assumption, in the present study, the photosensitive glasses containing both gold and K_2O in various amounts have been prepared and their crystallization temperatures and the crystalline phases separated out from the glasses have been determined by the DTA and X-ray diffraction technique.

EXPERIMENTAL

1) Preparation of Glass

Reagent grade Li_2CO_3, K_2CO_3 and SiO_2 were used for preparing the glasses, those batches of comositions were shown in Table 1. Photosensitive ingredients, Au and CeO_2, were added to the batches as HAuCl solution and CeO_2, respectively. After mixing thoroughly the batches were melted in sintered alumina crucibles with a capacity of 30 cc at 1320-1420°C for 2 hours in an electric furnace with silicon-carbide heating elements. This glass was poured directly on a steel plate and subsequently annealed at 500°C. Certain glasses of high alkali contents had a tendency to separate gold colloids upon cooling. For such glasses, a part of Li_2CO_3 in their batches was substituted by $LiNO_3$ to create oxidizing atmosphere during melting.

2) Formation of Gold Metal Nuclei

Ultraviolet exposure and subsequent heat-treatment are the necessary procedures for the development of colloid gold nuclei in photosensitive glasses. According to the experimental results of Maurer[6], the number of gold nuclei to be precipitated can be adjusted by the total dose of U.V. ray, i.e., the intensity of U.V. ray and duration of its exposure, but not by subsequent heat-

Table 1. Chemical composition and melting conditions of the glasses used.

	Glass composition (mole %)					Melting condition	
	Li_2O	SiO_2	K_2O	Au	CeO_2	Temp. (°C)	Time (hr.)
1	20	80	0	—	—	1420	2
2	20	80	1	—	—	1420	2
3	20	80	2	—	—	1420	2
4	20	80	3	—	—	1420	2
5	25	75	0	—	—	1400	2
6	25	75	1	—	—	1400	2
7	25	75	2	—	—	1400	2
8	25	75	3	—	—	1400	2
9	30	70	0	—	—	1350	2
10	30	70	1	—	—	1350	2
11	30	70	2	—	—	1350	2
12	30	70	3	—	—	1350	2
13	33	67	0	—	—	1320	2
14	33	67	1	—	—	1320	2
15	33	67	2	—	—	1320	2
16	33	67	3	—	—	1320	2
17	20	80	0	0.005	0.01	1420	2
18	20	80	1	0.005	0.01	1420	2
19	20	80	2	0.005	0.01	1420	2
20	20	80	3	0.005	0.01	1420	2
21	25	75	0	0.005	0.01	1400	2
22	25	75	1	0.005	0.01	1400	2
23	25	75	2	0.005	0.01	1400	2
24	25	75	3	0.005	0.01	1400	2
25	30	70	0	0.005	0.01	1350	2
26	30	70	1	0.005	0.01	1350	2
27	30	70	2	0.005	0.01	1350	2
28	30	70	3	0.005	0.01	1350	2
29	33	67	0	0.005	0.01	1320	2
30	33	67	1	0.005	0.01	1320	2
31	33	67	2	0.005	0.01	1320	2
32	33	67	3	0.005	0.01	1320	2

treatment conditions. Furthermore, according to Mie's theory[7], the glasses containing gold colloids of the same size and of the same number show the same light-absorption spectrum. In order to precipitate gold colloids of the same size and of the same number in all of the glass specimens prepared, in the present experiment, the glass specimens were exposed to the U.V. ray of constant intensity for such suitable time that after being subjected to the sunsequent heat-treatment, they will show the same light-absorption spectrum.

In practice, the following procedures were undertaken to find out the most suitable exposure time for each specimen. Several pieces of a glass were placed at a distance of 6 cm from a U.V. source (a 500 watts high pressure mercury

lamp) and exposed for various periods from 30 to 1000 min. All the exposed glasses were then heated at a rate of 5°C per minute from 200°C to the development temperature near 500°C in a regular furnace with automatic temperature control equipments and held at that temperature for 30 min. After cooling, all the specimens were subjected to the absorption spectrum analysis so that only the specimens whose absorption spectra were close to the one shown Fig. 1 were selected for further experiments. The ultraviolet exposure conditions for such specimens are listed in Table 2.

3) Determination of Crystallization Temperature

The precipitation of a crystal phase from its parent glass is usually accom-

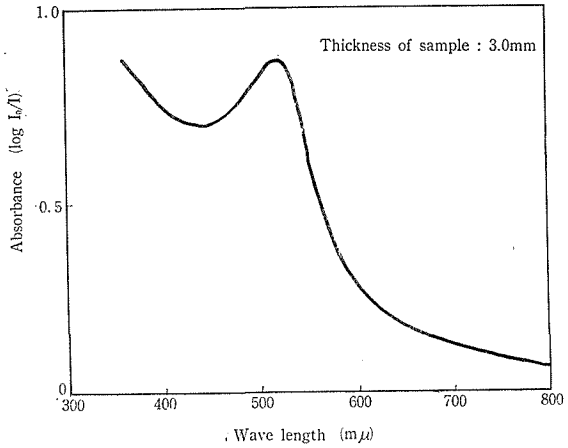

Fig. 1. Light-absorption spectrum of the glasses coloured by gold colloid.

Table 2. U. V. exposure and development conditions for sepapating out gold colloid in each glass.

Glass composition No.	U. V. Exposure time (min.)	Development condition	
		Temperature (°C)	Time (min.)
17	100	520	30
18	80	520	30
19	50	520	30
20	30	520	30
21	250	520	30
22	200	520	30
23	150	520	30
24	100	520	30
25	600	510	30
26	500	510	30
27	400	510	30
28	250	510	30
29	1000	500	30
30	800	500	30
31	600	500	30
32	400	500	30

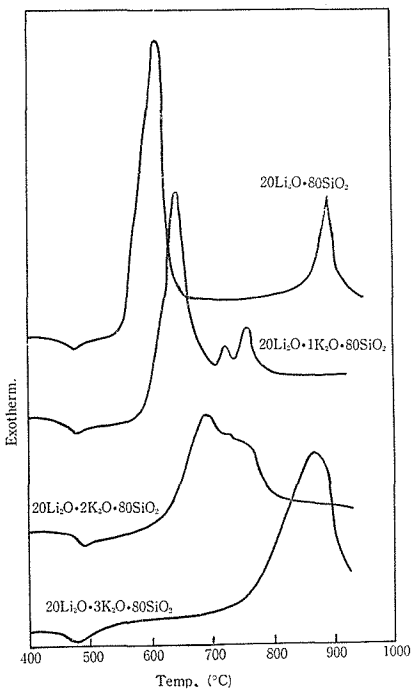

Fig. 2. Differential thermal analysis curves (1).

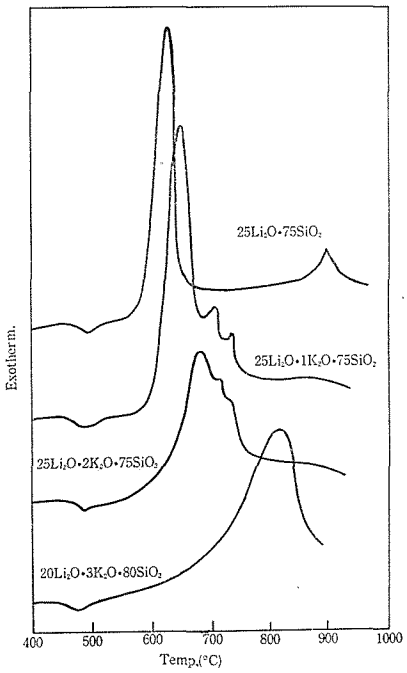

Fig. 3. Differential thermal analysis curves (2).

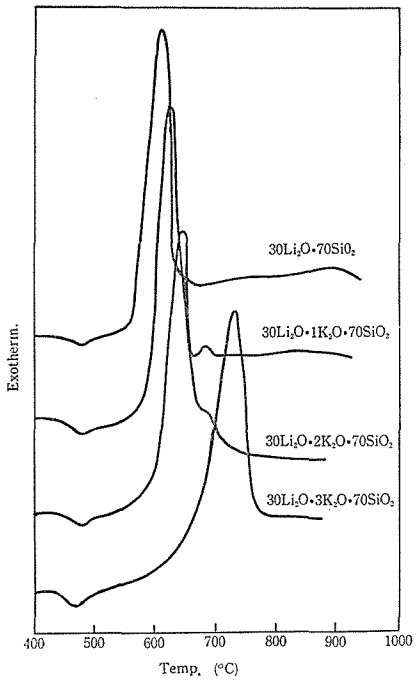

Fig. 4. Differential thermal analysis curves (3).

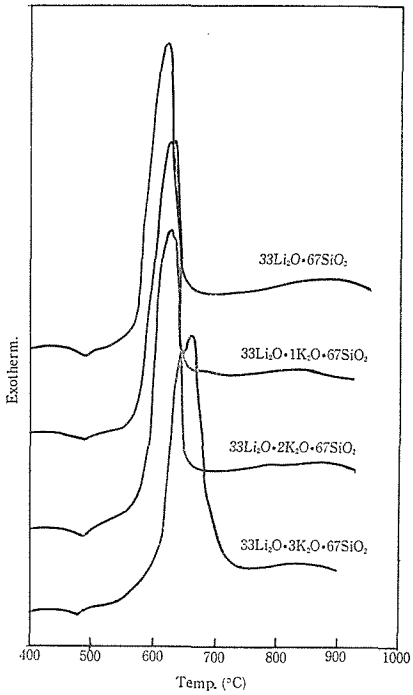

Fig. 5. Differential thermal analysis curves (4).

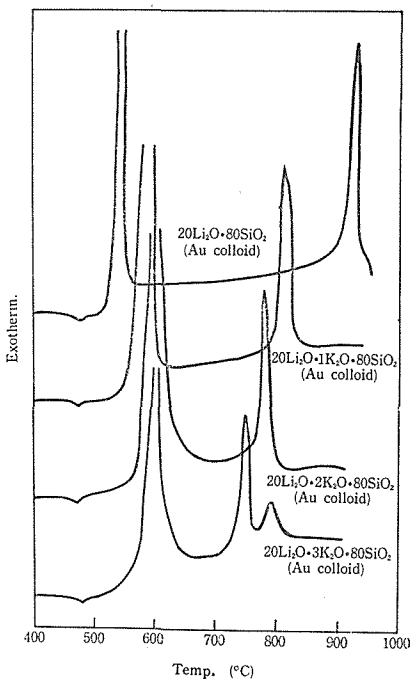

Fig. 6. Differential thermal analysis curves (5).

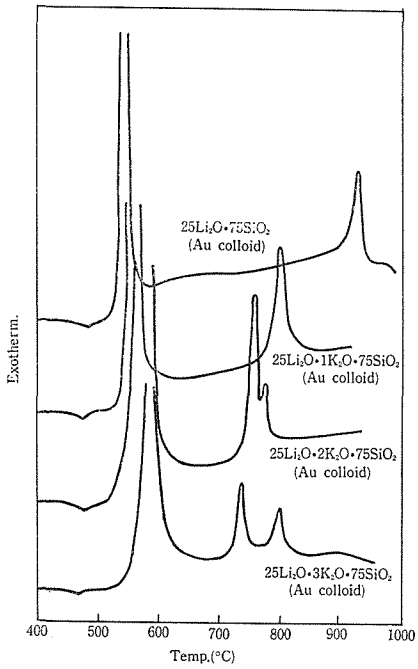

Fig. 7. Differential thermal analysis curves (6).

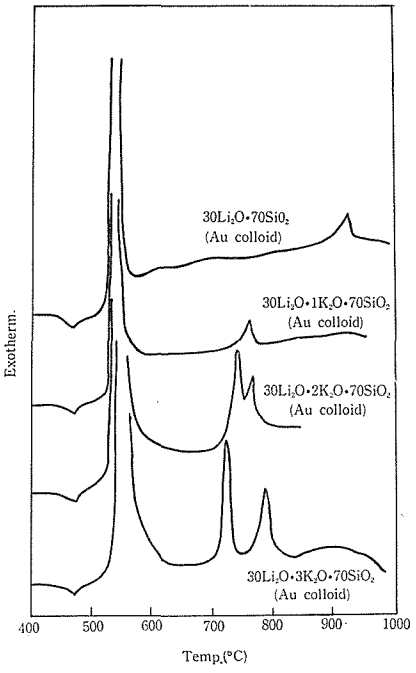

Fig. 8. Differential thermal analysis curves (7).

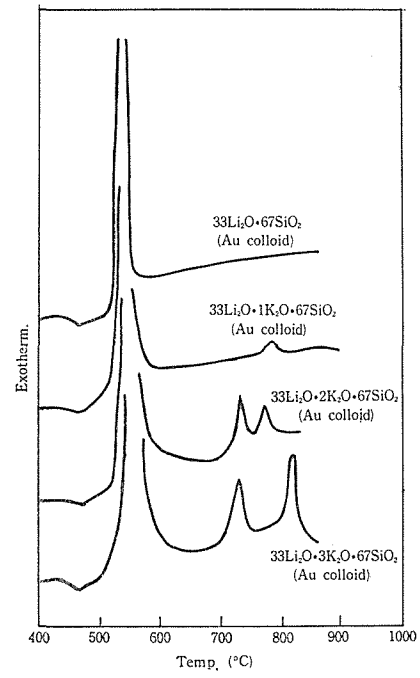

Fig. 9. Differential thermal analysis curves (8).

panied by the evolution of heat and, therefore, the differential thermal analysis (DTA) can be applied to the determination of its crystallization temperature. It should be mentioned, however, that the crystallization temperature obtained differs depending on the shape of the sample used: When the glass sample is in the powder form the crystallization temperature obtained is much lower than that obtained for the glass in a block, because the crystallization commences much faster at the glass surface than in the glass body. The crystallization temperature to be determined in the present study is of the body of the glass but not of its surface. Therefore, the glasses were formed into a slab 3×5×10 mm. in dimension and used as specimens for DTA. For measuring the temperature of specimens, a small hole was made in each specimens, in which a chromel alumel thermocouple was inserted. Alumina powders, as a reference material in DTA, that previously fired up to 1400°C were used. The heating rate was in all cases 5°C per minuite.

The results of DTA for all glasses are shown in Fig. 2 to 9. Furthermore, in order to compare the crystallization tendency of all the glasses, the temperature at which the first exothermal peak appears in the DTA curve was designated as the "crystallization temperature".

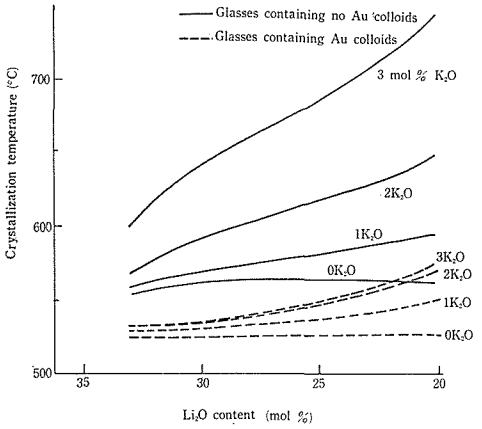

Fig. 10. Li_2O content *vs.* crystallization temperature of glasses.

The effects of gold colloids, Li_2O and K_2O content in the glass on the crystallization temperature can be seen more clearly in Fig. 10 where the crystallization temperature is plotted against the Li_2O content with various K_2O contents. It is obvious that the crystallization temperature is greatly influenced by both K_2O and Li_2O content. For the same amount of K_2O, the crstallization temperature rises as the Li_2O content decreases with an exception of the glasses containing no K_2O. The effect of K_2O is more apparent in the glasses without gold colloid than in those with gold colloids.

When the glass contains both gold colloids and K_2O, especially in large amount, three exothermal peaks appeared in the DTA curve. X-ray diffraction analysis of this glass revealed that the first exothermal peak is due to the pre-

cipitation of Li_2SiO_3, the second to the transformation from Li_2SiO_3 to $Li_2Si_2O_5$ and the third to the precipitation of SiO_2 phase.

4) **Determination of Crystal Phases**

The glass specimens were heated at a rate of 5°C/min. from room temperature up to the temperatures 10°C higher than their crystallization temperatures shown in Fig. 10 and kept for 30 min.. After cooled to room temperature they were subjected to X-ray diffraction analysis using a Shimazu diffractometer RX-2A utilizing Cu-Kα radiation. The results are summarized in Table 3. The weight proportion of Li_2SiO_3 to $Li_2Si_2O_5$ in Table 3 was estimated from the intensities of diffraction peaks due to Li_2SiO_3 and $Li_2Si_2O_5$. When only the peaks

Table 3. Crystalline phases separated out primarily from the glasses used.

Glass composition No.	Catalyst	Heat-treatment Temp. (°C)	Relative amount of crystallite	
			$Li_2Si_2O_5$	Li_2SiO_3
1	no	580	100	0
2	no	610	100	0
3	no	660	100	0
4	no	760	100	0
5	no	580	100	0
6	no	610	100	0
7	no	640	100	0
8	no	700	100	0
9	no	580	100	0
10	no	600	100	0
11	no	620	100	0
12	no	660	100	0
13	no	580	100	0
14	no	590	100	0
15	no	590	100	0
16	no	610	100	0
17	gold	540	100	0
18	gold	550	100	tr.
19	gold	570	40	60
20	gold	580	0	100
21	gold	540	100	0
22	gold	540	100	tr.
23	gold	550	50	50
24	gold	550	0	100
25	gold	540	100	0
26	gold	540	100	0
27	gold	540	70	30
28	gold	540	0	100
29	gold	540	100	0
30	gold	540	100	0
31	gold	540	90	10
32	gold	540	tr.	100

of Li_2SiO_3 were observed, a value of 100 was given to Li_2SiO_3 and 0 to $Li_2Si_2O_5$. Fig. 11 shows typical examples which were designated as the proportion of Li_2SiO_3 to $Li_2Si_2O_5$ being 0 to 100, 50 to 50 and 100 to 0, respectively. From Table 3 it is evident that Li_2SiO_3 precipitates only from the glass containing both gold colloids and K_2O_2 whereas $Li_2Si_2O_5$ precipitates primarily from the glass containing either gold colloids or K_2O. The proportion of Li_2SiO_3 to $Li_2Si_2O_5$ increases as K_2O content increases and reaches 100% when K_2O content becomes 3 mole%.

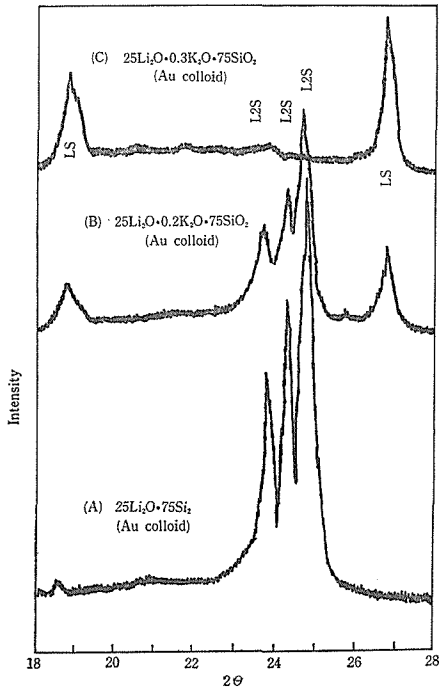

Fig. 11. X-ray diffraction patterns of the crystallized lithium silicate glasses containing K_2O and gold colloid.

DISCUSSION

1) The Effect of K_2O on the Crystallization of Lithium Silicate Glasses

Fig. 10 indicates that the addition of K_2O to lithium silicate glasses retards their crystallization irrespective of the presence of gold colloid nuclei. Its reasoning has already been presented in the paper by Sakka and Tashiro[3], which is based on the concept that the O-Si bonds in the Li-O-Si groups are strengthend by the introduction of single bonded oxygen ions associated with kalium ions: For the crystallization of lithium silicate glasses, the breakening of the Si-O bond in the Li-O-Si groups is the first requirement. When the single bonded oxygens associated with the K^{+1} ions are broght near to the Li^{+1} ions, the attraction of the oxygens toward the Li^{+1} ions in the Li-O-Si groups is weakened because the Li^{+1} ions are well screened by the oxgen associated with the K^{+1} ions, and consequently the O-Si bonds in the Li-O-Si groups are strengthened, resulting in the

delay of crystallization of glasses.

If this concept accepted, each Li^{+1} ions would receive more screening effect with increasing K_2O/Li_2O ratio in the compositions of glasses, and consequently the crystallization temperature of the glasses would increase with increasing their K_2O/Li_2O ratios. This expectation is actually found in Fig. 10: For instance, the two glasses of the compositions, $2K_2O \cdot 20Li_2O \cdot 80SiO_2$ and $3K_2O \cdot 30Li_2O$. $70SiO_2$, have the same crystallization temperature (640°C).

2) The Effect of Gold Colloids on the Crystallization of Lithium Silicate Glasses

The effect of gold colloid in decreasing the crystallization temperature of the glasses is obvious from Fig. 10 shown. Another interesting phenomenon is that the Li_2SiO_3 crystal separates out from the glasses which contain both glold colloids and K_2O. These two phenomena could be explained if the gold colloids have following two effects; an effect of lowering the activation energy for nucleation and of attracting lithium oxides on its surface.

a) An effect of lowering the activation energy for nucleation. According to the report resulted by Turnbull[8], the rate of formation of nuclei on the surface of a catalyst is represented by the formula,

$$J_c = A \exp[-(\Delta F f(\theta) + q)/kT]$$

in which F is the maximum free energy for formation of a nucleus on the surface of a catalyst, q being the activation free energy for diffusion of molecules across the phase boundary, $f(\theta)$ the function representing the reduction of the interfacial energy due to wetting of the catalyst surface by the cryslals precipitated on it where θ is the contact angle between the surface of catalyst and the crystals precipitated on it.

As already mentioned by Stookey[5] a lattice parameter of gold metal (4.070Å) is fairly close to one of those of Li_2SiO_3 crystal (4.66Å), it can be expected that the value of $f(\theta)$ in the above equation be low enough so that the crystallization commences from fairly low temperatures.

b) An effect of gold colloid in attracting lithium oxides. For the explanation of the formation of Li_2SiO_3 crystal, it has been proposed by the authors with introducing the concept that the gold colloid tends to attract the Li_2O, especially the polarizable oxygen ions associated with the Li^{+1} ions, towards its surface for its screening: The surface of the metal colloids has high surface free energy especially when their size is small, and cosequently requires to be surrounded by polarizable ions such as single bonded oxygen ions. This concept has first been proposed by Weyl[9] and later used by Rindone[1] for explanation of the formation of $Li_2Si_2O_3$ crystal on the surface of platinum colloids. By this adsorption process the Li_2O concentration near the surface of gold colloids increases, resulting in the precipitation of the Li_2SiO_2 crystal whose Li_2O content is much higher than that of the original glass composition.

3) Schematic Representation of the Role of Gold Colloid and K_2O

Assuming the two effects described above, the role of gold colloid and K_2O

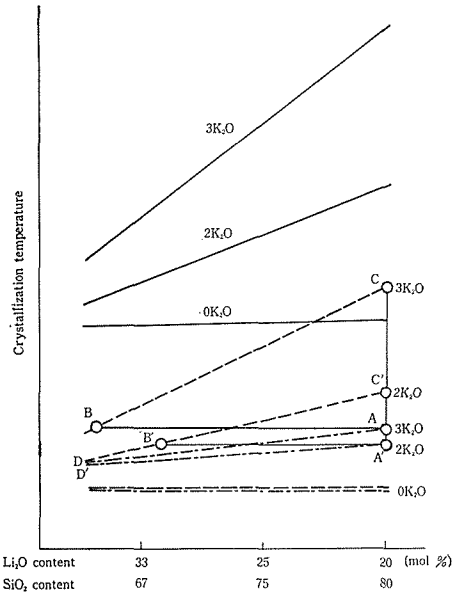

Fig. 12. Schematic representations of the crystallization temperatures of lithium silicate glasses containing no or small amounts of K_2O and gold colloids.

in loweing the crystallization temperature of the glasses and also in forming the Li_2SiO_3 crystal could be represented schematically as follows: The solid lines in Fig. 12 represent the relation between the Li_2O content of the glasses containing no gold nuclei and their crystallization temperature, which are drawn on the basis of the assumption that the crystallization temperature increases in proportion to the K_2O/Li_2O ratio as described above. If one further assumes that the catalyst which is capable of making $f(\theta)=0$ in the above equation exist in the glasses, the total energy barrier for crystallization will decrease and consequently the shifts of crystallization temperature would occur from the solid lines to the dotted lines, each corresponding to the same K_2O contents.

If one makes one more assumption that the composition of the glass near the surface of gold colloids become richer in the Li_2O content because of the screening demand of the surface, the crystallization temperature of the glasses would shift still more to that represented by the chain lines: For instance, the crystallization temperature of the $3K_2O\cdot 20Li_2O\cdot 80SiO_2$ glass with gold colloids would be represented by a point C in Fig. 12 if only the wetting effect of gold colloid be admitted. If one further admit the change of its composition toward the K_2O-rich region such as represented by a point B, the crystallization of the glass would take place at lower temperature as represented by a point A (the same temperature as represented by B). By considering the same way, the dotted line, C-B, could be shifted to the place represented by a chain line, A-D. The composition of the crystal formed at the point A should be Li_2SiO_3 but not $Li_2Si_2O_5$, because it is separated out from the glass near the surface of gold colloids whose Li_2O content is higher than that of the Li_2SiO_5 composition. The same shift could also be expected for the crystallization temperature lines of

the glasses containing none and 2 mol K_2O respectively. In theses two cases, however, the K_2O content of the glass at the surface of gold colloid would not exceed that of the $Li_2Si_2O_5$ composition as indicated by a point, B′, and thus the composition of the crystal to be separated out would be $Li_2Si_2O_5$. The fact that the Li_2SiO_3 crystal is separed out only when the K_2O content of the glass is high could thus be explained.

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